(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 471 372 B1

(12) EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention of the grant of the patent:
21.11.2001 Bulletin 2001/47

(51) Int Cl.[7]: **C07D 277/32**, A01N 47/44, C07D 213/61

(21) Application number: **91113705.7**

(22) Date of filing: **15.08.1991**

(54) Novel substituted guanidine derivatives, their preparation and use

Substituierte Guanidinderivate, ihre Herstellung und Anwendung

Guanidines substituées, leur préparation et leur utilisation

(84) Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL SE

(30) Priority: **17.08.1990 JP 21735690**
20.08.1990 JP 21962890
15.10.1990 JP 27662890
01.03.1991 JP 3610891
16.05.1991 JP 11198791

(43) Date of publication of application:
19.02.1992 Bulletin 1992/08

(73) Proprietor: **Takeda Chemical Industries, Ltd.**
Chuo-ku, Osaka (JP)

(72) Inventors:
- **Minamida, Isao**
  Tsukuba, Ibaraki 305 (JP)
- **Kando, Yasuyuki**
  Tsukuba, Ibaraki 305 (JP)
- **Ishizuka, Hitoshi**
  Tsukuba, Ibaraki 305 (JP)
- **Okauchi, Tetsuo**
  Hirakata, Osaka 573 (JP)
- **Uneme, Hideki**
  Tsukuba, Ibaraki 305 (JP)

(74) Representative:
von Kreisler, Alek, Dipl.-Chem. et al
Patentanwälte
von Kreisler-Selting-Werner
Postfach 10 22 41
50462 Köln (DE)

(56) References cited:
EP-A- 0 302 833
EP-A- 0 375 907
EP-A- 0 376 279

EP 0 471 372 B1

Printed by Jouve, 75001 PARIS (FR)

$$R^7R^8NH \quad [X],$$

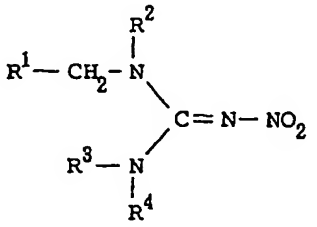
or

$$R^{11}R^{12}NH \quad [XI],$$

wherein each group has the same meaning as defined above.

Claims for the following Contracting State : ES

1. A process for preparing a substituted nitroguanidine compound of the formula [I]:



[I]

wherein R^1 is a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different,
and are selected from C_{1-15} alkyl group, C_{3-10} cycloalkyl group, C_{2-10} alkenyl group, C_{2-10} alkynyl group, C_{3-10} cycloalkenyl group, C_{6-10} aryl group, C_{7-10} aralkyl group, phenethyl group, nitro, hydroxy, mercapto, oxo, thioxo, cyano, carbamoyl, carboxyl, C_{1-4} alkoxycarbonyl, sulfo, halogen, C_{1-4} alkoxy group, C_{6-10} aryloxy group, C_{1-4} alkylthio group, C_{6-10} arylthio group, C_{1-4} alkylsulfinyl group, C_{6-10} arylsulfinyl group, C_{1-4} alkylsulfonyl group, C_{6-10} arylsulfonyl group, amino, C_{2-6} acylamino group, mono- or di-C_{1-4} alkylamino group, C_{3-6} cycloalkylamino group, C_{6-10} arylamino group, C_{2-4} acyl group, C_{6-10} arylcarbonyl group and five- to six-membered heterocyclic group each containing 1 to 4 heteroatoms selected from oxygen, sulfur and nitrogen,
and the above C_{3-10} cycloalkyl, C_{3-10} cycloalkenyl, C_{6-10} aryl, C_{7-10} aralkyl, C_{6-10} aryloxy, C_{6-10} arylthio, C_{6-10} arylsulfinyl, C_{6-10} arylsulfonyl, C_{6-10} arylamino or heterocyclic group may be substituted with 1 to 5 substituent groups which may be the same or different selected from halogen, hydroxyl, C_{1-4} alkyl, C_{2-4} alkenyl, C_{2-4} alkynyl, C_{6-10} aryl, C_{1-4} alkoxy, C_{1-4} alkylthio and phenylthio, and the above C_{1-15} alkyl group, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{1-4} alkoxy, C_{1-4} alkylthio, C_{1-4} alkylsulfinyl, C_{1-4} alkylsulfonyl, amino, mono- or di-C_{1-4} alkylamino or C_{3-6} cycloalkylamino may be substituted with 1 to 5 substituent groups which may be the same or different selected from halogen, hydroxyl, C_{1-4} alkoxy and C_{1-4} alkylthio,

R^2 is cyano,

a group of the formula: $-S(O)_n-R^{13}$
wherein n is an integer of 1 or 2 and R^{13} is a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1,
a group of the formula: $-P(=O)R^{14}R^{15}$
wherein R^{14} and R^{15} are each independently hydroxyl; a hydrocarbon group attached through an oxygen atom selected from C_1-C_{15} alkoxy, C_3-C_{10} cycloalkoxy, C_2-C_{10} alkenyloxy, C_2-C_{10} alkynyloxy, C_3-

C_{10} cycloalkenyloxy, C_6-C_{10} aryloxy or C_7-C_{10} aralkyloxy, this hydrocarbon group optionally having 1 to 5 substituents and are defined as above for R^1; a heterocyclyloxy group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1; a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents and are ; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1;

a group of the formula: -CO-OR^6

wherein R^6 is a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1, or

a group of the formula: -CO-NR^7R^8

wherein R^7 and R^8, which are the same or different, are each independently hydrogen; a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1; or R^7 and R^8, taken together with the nitrogen atom to which they are attached are a cyclic amino group, which may be substituted with 1 to 4 C_{1-4} alkyl groups;

R^3 is hydrogen,

cyano,

a hydrocarbon group selected from C_1-C_{15} alkyl, C_2-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_3-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1(except for one substituted with an oxo group at the binding site),

a group of the formula: -$S(O)_n$-R^{13}

wherein n is an integer of 0, 1 or 2 and R^{13} is a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1;

a group of the formula: -$P(=O)R^{14}R^{15}$

wherein R^{14} and R^{15} are each independently hydroxyl; a hydrocarbon group attached through an oxygen atom, selected from C_1-C_{15} alkoxy, C_3-C_{10} cycloalkoxy, C_2-C_{10} alkenyloxy, C_2-C_{10} alkynyloxy, C_3-C_{10} cycloalkenyloxy, C_6-C_{10} aryloxy or C_7-C_{10} aralkyloxy, this hydrocarbon group optionally having 1 to 5 substituents defined as above for R^1 ; a heterocyclyloxy group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1; a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_2-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1,

a group of the formula: -CO-R^9

wherein R^9 is hydrogen; a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally hav-

ing 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1,

a group of the formula: -CO-OR^{10}

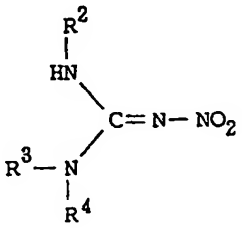
wherein R^{10} is a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1, or

a group of the formula: -CO-$NR^{11}R^{12}$

wherein R^{11} and R^{12}, which are the same or different, are each independently hydrogen; a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents defined as above for R^1; or a heterocyclic group having a single or fused ring with 5 to 8 ring members in each ring and having from one to five heteroatoms in each ring independently selected from oxygen, nitrogen and sulfur, wherein said heterocyclic group may optionally be substituted with 1 to 5 substituents which may be the same or different and are defined as above for R^1; or R^{11} and R^{12}, taken together with the nitrogen atom to which they are attached are a cyclic amino group, which may be substituted with 1 to 4 C_{1-4} alkyl groups; and

R^4 is hydrogen or a C_1-C_4 alkyl group; or a salt thereof,

which comprises reacting a compound of the formula [IV]:



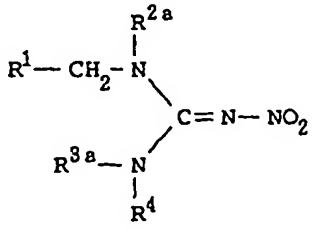
[IV]

wherein each group has the same meaning as defined above, or a salt thereof, with a compound of the formula [V]:

$$R^1—CH_2—Y \qquad [V]$$

wherein R^1 has the same meaning as defined above and Y is a leaving group.

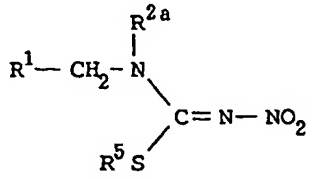
2. A process for preparing a substituted nitroguanidine compound of the formula [I^a]:



[I^a]

wherein

R^1 and R^4 are as defined in claim 1
R^{2a} corresponds to R^2 as defined in claim 1,
R^{3a} is hydrogen or a hydrocarbon group selected from C_{1-15} alkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{3-10} cycloalkenyl, C_{6-10} aryl or C_{7-10} aralkyl, this group optionally having 1 to 5 substituents as defined in claim 1 for R^1, or a salt thereof,
which comprises reacting a compound of the formula [II]:



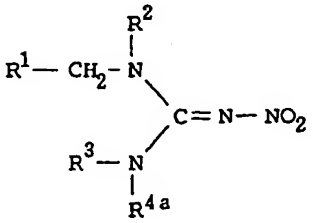
[II]

wherein R^1 and R^{2a} have the same meanings as defined above and R^5 is a substituted or unsubstituted hydrocarbon group or a substituted or unsubstituted acyl group, or a salt thereof, with a compound of the formula [III]:

$$R^{3a}R^4NH \qquad [III]$$

wherein R^{3a} and R^4 have the same meanings as defined above, or a salt thereof.

3. A process for preparing a substituted nitroguanidine compound of the formula [I^b]:

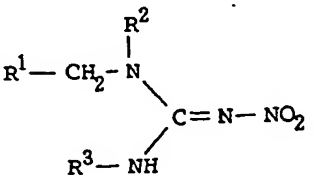


[I^b]

wherein

R^1, R^2 and R^3 are as defined in claim 1,
R^{4a} is a C_1-C_4 alkyl group; or a salt thereof,

which comprises reacting a compound of the formula [I^c]:



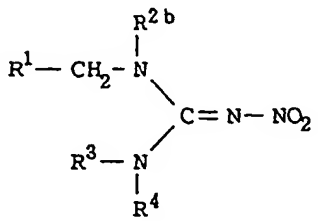
[I^c]

wherein each group has the same meaning as defined above, or a salt thereof, with a compound of the formula [VI]:

$$R^{4a}—Y \qquad [VI]$$

wherein each group has the same meaning as defined above.

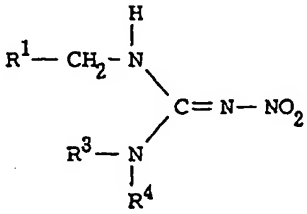
4. A process for preparing a substituted nitroguanidine compound of the formula [I^d]:



[I^d]

wherein

R^1, R^3 and R^4 are as defined in claim 1
R^{2b} corresponds to R^2 as defined in claim 1, or salt thereof, which comprises reacting a compound of the formula [I^e]:



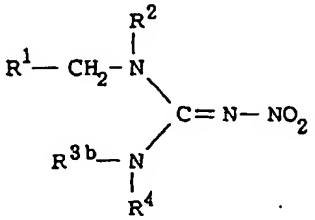
[I^e]

wherein each group has the same meaning as defined above, or a salt thereof, with a compound of the formula [VII]:

$$R^{2b}—Y \qquad [VII]$$

wherein each group has the same meaning as defined above.

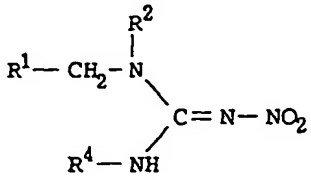
5. A process for preparing a substituted nitroguanidine compound of the formula [I^f]:



[I^f]

wherein R^1, R^2 and R^4 have the same meanings as defined in claim 1 and R^{3b} is cyano,
a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cy-

cloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents as defined in claim 1 for R^1 (except for one substituted with an oxo group at the binding site),
a group of the formula: $-S(O)_n-R^{13}$ as defined in claim 1, a group of the formula: $-P(=O)R^{14}R^{15}$ as defined in claim 1, a group of the formula: $-CO-R^9$ as defined in claim 1, a group of the formula: $-CO-OR^{10}$ as defined in claim 1, a group of the formula: $-CO-NR^{11}R^{12}$ as defined in claim 1 or a salt thereof,
which comprises reacting a compound of the formula [Ig]:



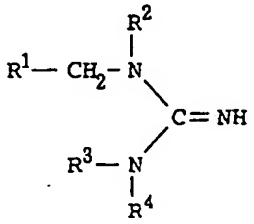
[I^g]

wherein each group has the same meaning as defined above, or a salt thereof, with a compound of the formula [VIII]:

[VIII]

wherein each group has the same meaning as defined above.

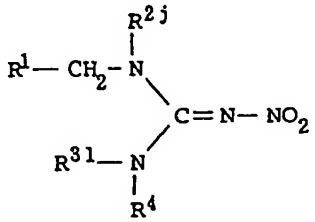
6. A process for preparing a substituted nitroguanidine compound of the formula [I] according to Claim 1 or a salt thereof, which comprises reacting a compound of the formula [IX]:



[IX]

wherein each group has the same meaning as defined above, or a salt thereof, with a nitrating reagent.

7. A process for preparing a substituted nitroguanidine compound of the formula [Ir]:

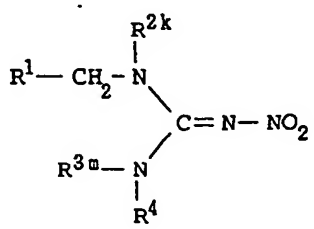


[I^r]

wherein

R^1 and R^4 have the same meanings as defined in claim 1, and
R^{2j} : corresponds to R^2 as defined in claim 1
R^{3l} corresponds to R^3 as defined in claim 1,

provided that at least one of R^{2j} and R^{3l} is the substituted or unsubstituted aminocarbonyl group as defined above; or a salt thereof,
which comprises reacting a compound of the formula [I^s]:



[I^s]

wherein

R^1 and R^4 have the same meanings as defined above, and

R^{2k} corresponds to R^2 as defined above

R^{3m} corresponds to R^3 as defined above,

provided that at least one of R^{2k} and R^{3m} is a reactive ester which is -CO-OR^6 or -CO-OR^{10}, respectively; or a salt thereof, with a compound of the formula :

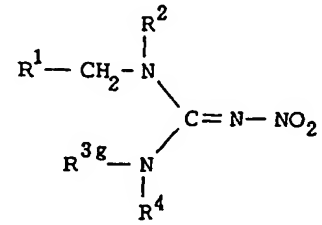
$$R^7R^8NH \qquad [X],$$

or

$$R^{11}R^{12}NH \qquad [XI],$$

wherein each group has the same meaning as defined above.

8. The process according to claim 1 in which the compound is represented by the formula:



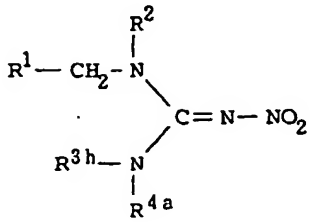
[I^j]

wherein

R^1, R^2 and R^4 are as defined in claim 1
R^{3g} is hydrogen or a hydrocarbon group selected from C_1-C_{15} alkyl, C_3-C_{10} cycloalkyl, C_2-C_{10} alkenyl, C_2-C_{10} alkynyl, C_3-C_{10} cycloalkenyl, C_6-C_{10} aryl or C_7-C_{10} aralkyl, this group optionally having 1 to 5 substituents as defined in claim 1 for R^1 (except for one substituted with an oxo group at the binding site),

or a salt thereof.

9. The process according to claim 1 in which the compound is represented by the formula:



[I^1]

wherein

R^1 and R^2 are as defined in claim 1

R^{3h}, is hydrogen, and R^{4a} is a C_1-C_4 alkyl group;

or a salt thereof.

10. The process according to claim 1, in which the heterocyclic group R^1 is a five- or six-membered nitrogen-containing heterocyclic group.

11. The process according to claim 1 in which the heterocyclic group R^1 is 2- or 3-thienyl, 2- or 3-furyl, 2- or 3-pyrrolyl, 2-, 3- or 4-pyridyl, 2-, 4- or 5-oxazolyl, 2-, 4- or 5-thiazolyl, 3-, 4- or 5-pyrazolyl, 2-, 4- or 5-imidazolyl, 3-, 4- or 5-isoxazolyl, 3-, 4- or 5-isothiazolyl, 3- or 5-(1,2,4-oxadiazolyl), 1,3,4-oxadiazolyl, 3- or 5-(1,2,4-thiadiazolyl), 1,3,4-thiadiazolyl, 4- or 5-(1,2,3-thiadiazolyl), 1,2,5-thiadiazolyl, 1,2,3-triazolyl, 1,2,4-triazolyl, 1H- or 2H-tetrazolyl, N-oxide of 2-, 3- or 4-pyridyl, 2-, 4- or 5-pyrimidinyl, N-oxide of 2-, 4- or 5-pyrimidinyl, 3- or 4-pyridazinyl, pyrazinyl, N-oxide of 3- or 4-pyridazinyl, benzofuryl, benzothiazolyl, benzoxazolyl, triazinyl, oxotriazinyl, tetrazolo[1,5-b]pyridazinyl, triazolo[4,5-b]-pyridazinyl, oxoimidazolyl, dioxotriazinyl, pyrrolidinyl, piperidyl, pyranyl, thiopyranyl, 1,4-oxazinyl, morpholinyl, 1,4-thiazinyl, 1,3-thiazinyl, piperazinyl, benzoimidazolyl, quinolyl, isoquinolyl, cinnolinyl, phthalazinyl, quinazolinyl, quinoxalinyl, indolizinyl, quinolizinyl, 1,8-naphthyridinyl, purinyl, pteridinyl, dibenzofuranyl, carbazolyl, acridinyl, phenanthridinyl, phenazinyl, phenothiazinyl, or phenoxazinyl.

12. The process according to claim 1 , wherein R^1 is a five- or six-membered nitrogen containing heterocyclic group which is substituted with 1 to 5 substituents selected from C_{1-15} alkyl; C_{3-10} cycloalkyl; C_{2-10} alkenyl; C_{2-10} alkynyl; C_{3-10} cycloalkenyl; C_{6-10} aryl; C_{7-10} aralkyl; nitro; hydroxyl; mercapto; oxo; thioxo; cyano; carbamoyl; carboxyl; C_{1-4} alkoxycarbonyl; sulfo; halogens; C_{1-4} alkoxy; C_{6-10} aryloxy; C_{1-4} alkylthio; C_{6-10} arylthio; C_{1-4} alkylsulfinyl; C_{6-10} arylsulfinyl; C_{1-4} alkylsulfonyl; C_{6-10} arylsulfonyl; amino; C_{2-6} acylamino; mono- or di-C_{1-4} alkylamino; C_{6-10} arylamino; C_{2-4} acyl; C_{6-10} arylcarbonyl; 2- or 3-thienyl; 2- or 3-furyl; 3-, 4- or 5-pyrazolyl; 2-, 4- or 5-thiazolyl; 3-, 4- or 5-isothiazolyl; 2-, 4- or 5-oxazolyl; 3-,4- or 5-isoxazolyl; 2-, 4- or 5-imidazolyl; 1,2,3- or 1,2,4-triazolyl; 1H- or 2H-tetrazolyl; 2-, 3- or 4-pyridyl; 2-, 4-or 5-pyrimidinyl; 3- or 4-pyridazinyl; quinolyl; isoquinolyl; and indolyl.

13. The process according to claim 1 wherein R^1 is 2-, 3- or 4-pyridyl or 2-, 4- or 5-thiazolyl, which is substituted with 1 to 4 halogens.

14. The process according to claim 1 wherein R^3 is a C_{1-15} alkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{3-10} cycloalkenyl group.

15. The process according to claim 1 wherein R^3 is cyano,
a group of the formula: -CO-R^9 as defined in claim 1, a group of the formula: -CO-OR^{10} as defined in claim 1, or a group of the formula: -CO-$NR^{11}R^{12}$ as defined in claim 1.

16. The process according to claim 15, wherein R^9 is a C_{1-15} alkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, or C_{3-10} cycloalkenyl group.

17. The process according to claim 15, wherein R^3 is a group of the formula: -CO-OR^{10} as defined in claim 1.

18. The process according to claim 17, wherein R^{10} is C_{1-15} alkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{3-10} cycloalkenyl, C_{6-10} aryl or C_{7-10} aralkyl group.

19. The process according to claim 1 wherein R^3 is hydrogen; C_{1-4} alkyl; C_{1-7} acyl; C_{7-12} arylcarbonyl; C_{2-7} alkoxycarbonyl; C_{7-12} aryloxycarbonyl; C_{8-13} aralkyloxycarbonyl; C_{2-7} alkylaminocarbonyl; di-C_{1-4} alkylaminocarbonyl; saturated cyclic aminocarbonyl; or C_{1-4} alkylsulfonyl.

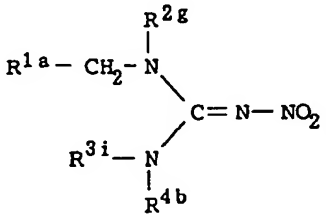
20. The process according to claim 1 wherein R^2 is cyano,
a group of the formula: -CO-OR^6 as defined in claim 1
or
a group of the formula: -CO-NR^7R^8 as defined in claim 1.

21. The process according to claim 20, wherein R^6 is C_{1-15} alkyl, C_{3-10} cycloalkyl, C_{2-10} alkenyl, C_{2-10} alkynyl, C_{3-10} cycloalkenyl, C_{6-10} aryl or C_{7-10} aralkyl group.

22. The process according to claim 1 wherein R^2 is C_{2-7} alkoxycarbonyl.

23. The process according to claim 1 wherein R^4 is C_{1-4} alkyl.

24. The process according to claim 1 in which the compound is represented by the formula:



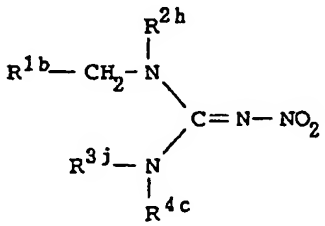
[I^n]

wherein

R^{1a} is pyridyl, halogenopyridyl, thiazolyl, or halogenothiazolyl,
R^{2g} is C_{2-7} alkoxycarbonyl, C_{7-12} aryloxycarbonyl, C_{8-13} aralkyloxycarbonyl, C_{2-7} alkylaminocarbonyl, di-C_{1-4} alkylaminocarbonyl, alicyclic aminocarbonyl, or C_{1-4} alkylsulfonyl,
R^{3i} is hydrogen, C_{1-4} alkyl, C_{7-12} arylcarbonyl, C_{7-12} aryloxycarbonyl, C_{8-13} aralkyloxycarbonyl, C_{2-7} alkylaminocarbonyl, di-C_{1-4} alkylaminocarbonyl, alicyclic aminocarbonyl, or C_{1-4} alkylsulfonyl, and
R^{4b} is hydrogen or C_{1-4} alkyl; or a salt thereof.

25. The process according to claim 24, wherein R^{1a} is halogenopyridyl or halogenothiazolyl.

26. The process according to claim 1 in which the compound is represented by the formula:



[I^n]

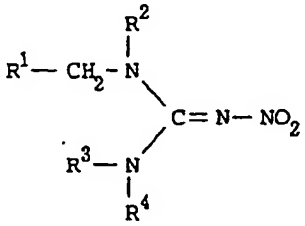
wherein R^{1b} is pyridyl, halogenopyridyl, thiazolyl, or halogenothiazolyl; R^{2h} is C_{2-7} alkoxycarbonyl; R^{3j} is hydrogen; and R^{4c} is methyl or ethyl; or a salt thereof.

27. The process according to claim 24 in which the compound or a salt thereof, is selected from

1-(2-chloro-5-thiazolylmethyl)-1-cyano-3,3-dimethyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-1,3-diphenoxycarbonyl-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)- 1-dimethylaminocarbonyl-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-3-methyl-1-morpholinocarbonyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-3,3-dimethyl-1-methanesulphonyl-2-nitroguanidine,

1-(2-chloro-5-thiazolylmethyl)-1-methoxycarbonyl-3-methyl-2-nitroguanidine,
1-(t-butoxycarbonyl)-1-(2-chloro-5-thiazolylmethyl)-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-1-ethoxycarbonyl-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-1-n-propoxycarbonyl-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-1-isopropoxycarbonyl-3-methyl-2-nitroguanidine,
1-(n-butoxycarbonyl)-1-(2-chloro-5-thiazolylmethyl)-3-methyl-2-nitroguanidine,
1-(isobutoxycarbonyl)-1-(2-chloro-5-thiazolylmethyl)-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-1-(1-chloroethoxycarbonyl)-3-methyl-2-nitroguanidine,
1-(2-chloro-5-thiazolylmethyl)-3-methyl-1-pyrrolidinocarbonyl-2-nitroguanidine, and
1-(2-chloro-5-thiazolylmethyl)-3-methyl-1-benzyloxycarbonyl-2-nitroguanidine.

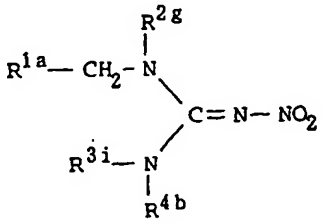
28. A pesticidal composition comprising an effective amount of the substituted nitroguanidine compound of the formula [I]:



[I]

wherein R^1, R^2 R^3 and R^4 are as defined in claim 1, or a salt thereof,
in admixture with an acceptable carrier, vehicle, diluent or excipient.

29. A pesticidal composition comprising an effective amount of a substituted nitroguanidine compound of the formula:



[I^p]

wherein

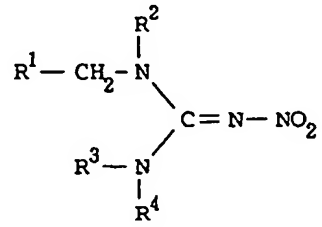
R^{1a} is pyridyl, halogenopyridyl, thiazolyl, or halogenothiazolyl,
R^{2g} is C_{7-12} aryloxythiocarbonyl,
R^{3i} is hydrogen, C_{1-4} alkyl, C_{7-12} arylcarbonyl, C_{7-12} aryloxycarbonyl, C_{8-13} aralkyloxycarbonyl, C_{2-7} alkylaminocarbonyl, di-C_{1-4} alkylaminocarbonyl, alicyclic aminocarbonyl, or C_{1-4} alkylsulfonyl, and
R^{4b} is hydrogen or C_{1-4} alkyl; or a salt thereof,

in admixture with an acceptable carrier, vehicle, diluent or excipient.

30. A pesticidal composition comprising an effective amount of the substituted nitroguanidine compound or a salt thereof made according to Claim 27 or a salt thereof in admixture with an acceptable carrier, vehicle, diluent or excipient.

31. A pesticidal composition comprising an effective amount of 1-(2-chloro-5-thiazolylmethyl)-3,3-dimethyl-2-nitro-1-phenoxythiocarbonylguanidine- or a salt thereof in admixture with an acceptable carrier, vehicle, diluent or excipient.

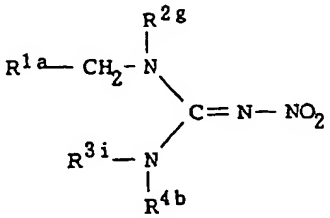
32. A use of a substituted nitroguanidine compound of the formula [I]:



[I]

wherein R^1, R^2, R^3 and R^4 are as defined in claim 1 or a salt thereof, for the manufacture of a pesticidal composition.

33. A use of a subsituted nitroguanidine of the formula:



[I^{III}]

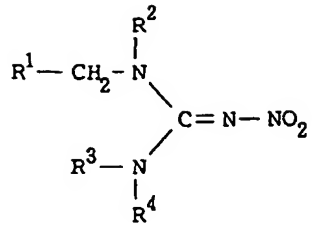
wherein

R^{1a} is pyridyl, halogenopyridyl, thiazolyl, or halogenothiazolyl, R^{2g} is C_{7-12} aryloxythiocarbonyl, R^{3i} is hydrogen, C_{1-4} alkyl, C_{7-12} arylcarbonyl, C_{7-12} aryloxycarbonyl, C_{8-13} aralkyloxycarbonyl, C_{2-7} alkylaminocarbonyl, di-C_{1-4} alkylaminocarbonyl, alicyclic aminocarbonyl, or C_{1-4} alkylsulfonyl, and R^{4b} is hydrogen or C_{1-4} alkyl; or a salt thereof for the manufacture of a pesticidal composition.

34. A use of a compound according to claim 33, wherein R^{1a} is halogenopyridyl or halogenothiazolyl.

35. A use of a compound according to claim 33 or a salt thereof which is 1-(2-chloro-5-thiazolylmethyl)-3,3-dimethyl-2-nitro1-phehoxythlocarbonylguanidine.

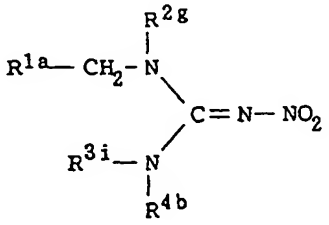
36. A method for controlling a pest which comprises applying an effective amount of a substituted nitroguanidine compound of the formula [I]:



[I]

wherein R^1, R^2, R^3 and R^4 are as defined in claim 1
or a salt thereof, to prevent said pest.

37. A method for controlling a pest which comprises applying an effective amount of a substituted nitroguanidine compound of the formula:



[I^m]

wherein

R^{1a} is pyridyl, halogenopyridyl, thiazolyl, or halogenothiazolyl,
R^{2g} is C_{7-12} aryloxythiocarbonyl,
R^{3i} is hydrogen, C_{1-4} alkyl, C_{7-12} arylcarbonyl, C_{7-12} aryloxycarbonyl, C_{8-13} aralkyloxycarbonyl, C_{2-7} alkylaminocarbonyl, di-C_{1-4} alkylaminocarbonyl, alicyclic aminocarbonyl, or C_{1-4} alkylsulfonyl, and
R^{4b} is hydrogen or C_{1-4} alkyl; or a salt thereof to prevent said pest.

38. A method according to claim 37, wherein R^{1a} is halogenopyridyl or halogenothiazolyl.

39. A method according to claim 37 wherein the compound is 1-(2-chloro-5-thiazolylmethyl)-3,3-dimethyl-2-nitro-1-phenoxythiocarbonylguanidine or a salt thereof.

Patentansprüche

Patentansprüche für folgende Vertragsstaaten : AT, BE, CH, DE, DK, FR, GB, GR, IT, LI, LU, NL, SE

1. Verbindung der Formel